FINAL REPORT

TRANSPORT ON FRACTAL NETWORKS

Nonr N00014-91-J-1063

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I. Introduction

The ONR Contract Nonr N00014-91-J-1063 brought to a conclusion our studies of the dyanmics of transport on fractal networks. In particular, we have made substantial progress towards understanding the ac conductivity of a fractal network [$(Na^+, Ba^{2+})\beta$"-alumina].

Mixed $(Na^+, Ba^{2+})\beta$"-alumina crystals are near ideal examples of ionic motion in a two dimensional percolating network. At low temperatures, the Na^+ ions move along a two dimensional percolation network in a "sea" of frozen Ba^{2+} ions, the latter blocking available sites for the Na^+ ions. For sufficient Ba^{2+} concentration, the number of available sites for Na^+ ion motion falls below p_c, the critical percolation concentration. This implies a vanishing dc conductivity. We had measured the extrapolated dc conductivity for a range of compositions and over a temperature range of 173K to 373K. The conductivity exhibits activated behavior, with an unusual dependence of the activation energy on (Na^+, Ba^{2+}) concentration. As seen in Fig. 1, the activation energy rises rapidly from the pure Na^+ and Ba^{2+} values to two "plateaus" of energy $\Delta = 0.48$ eV and $\Delta = 0.67$ eV, respectively. The plateaus cross over from one to the other between 40% and 50% Ba^{2+} exchange. We interpret the plateau values of Δ to be the "bare"-potential-well minima depths for the Na^+ and Ba^{2+} ions. The smaller values for the pure Na^+ and Ba^{2+} material are interpreted as the consequence of interplay between the single ion attractive potential and the inter-ionic repulsive Coulomb potential which results in a collective state. The competing interactions lead to off-site ionic positions, thereby reducing Δ from its "bare" value. The screening of the inter-ionic Coulumb interaction by the minority ions in the mixed materials allows the majority ions to move independently, thereby exhibiting the
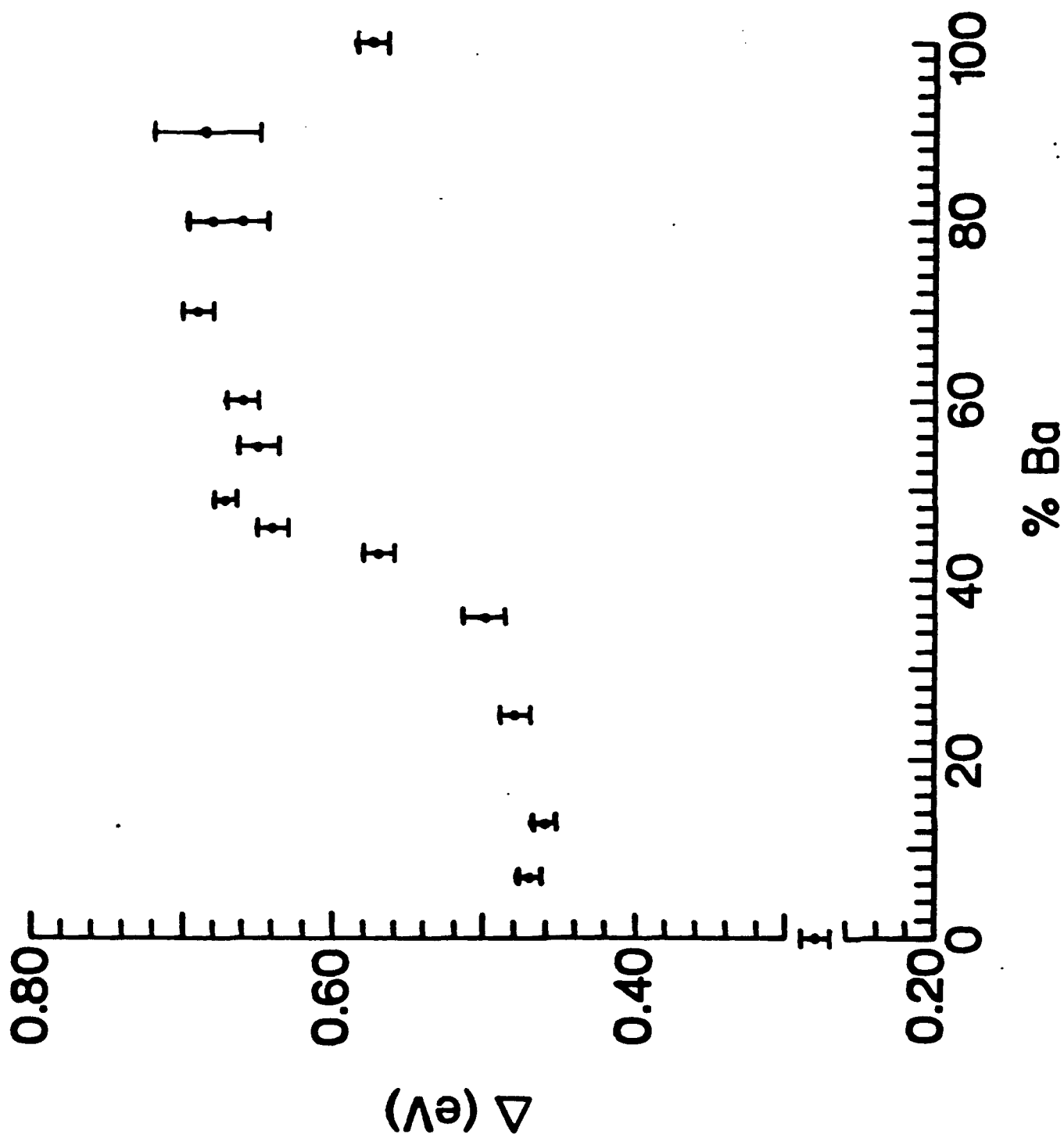
Fig. 1. Activation energies Δ extracted from the extrapolated dc

conductivity as a function of Ba^{2+} exchange.

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full "bare" value of Δ in conductivity measurements.

II. Results of Research Under Nonr N00014-91-J-1063

Our ac conductivity, $\sigma(\omega)$, measurements made during the contract period under Nonr N00014-91-J-1063 confirm this picture. We have measured $\sigma(\omega)$ from 10^4 to 10^7 Hz for temperatures between 150K and 440K. The Cole-Cole plots in the complex impedance plane are off-axis circles for the pure materials, but are on-axis for the mixed materials (except at the cross over concentration). Furthermore, the real part of $\sigma(\omega)$ is nearly independent of ω at frequencies of the order of the relaxation frequency for the mixed materials, while it exhibits power law behavior in the same range for the pure materials. Finally, the electric modulus, when plotted as a function of frequency is closer to an inverted "V", characteristic of simple Debye-like behavior, for the mixed as compared to the pure materials. Each of these results points to collective behavior in the pure materials and single particle behavior in the mixed materials.

ac conductivity measurements were made using a HP4192 LFIA. An average single crystal of β"-alumina has an effective capacitance of only $\sim 10^{-14}$ farads for frequencies of the order of the carrier hopping frequency.
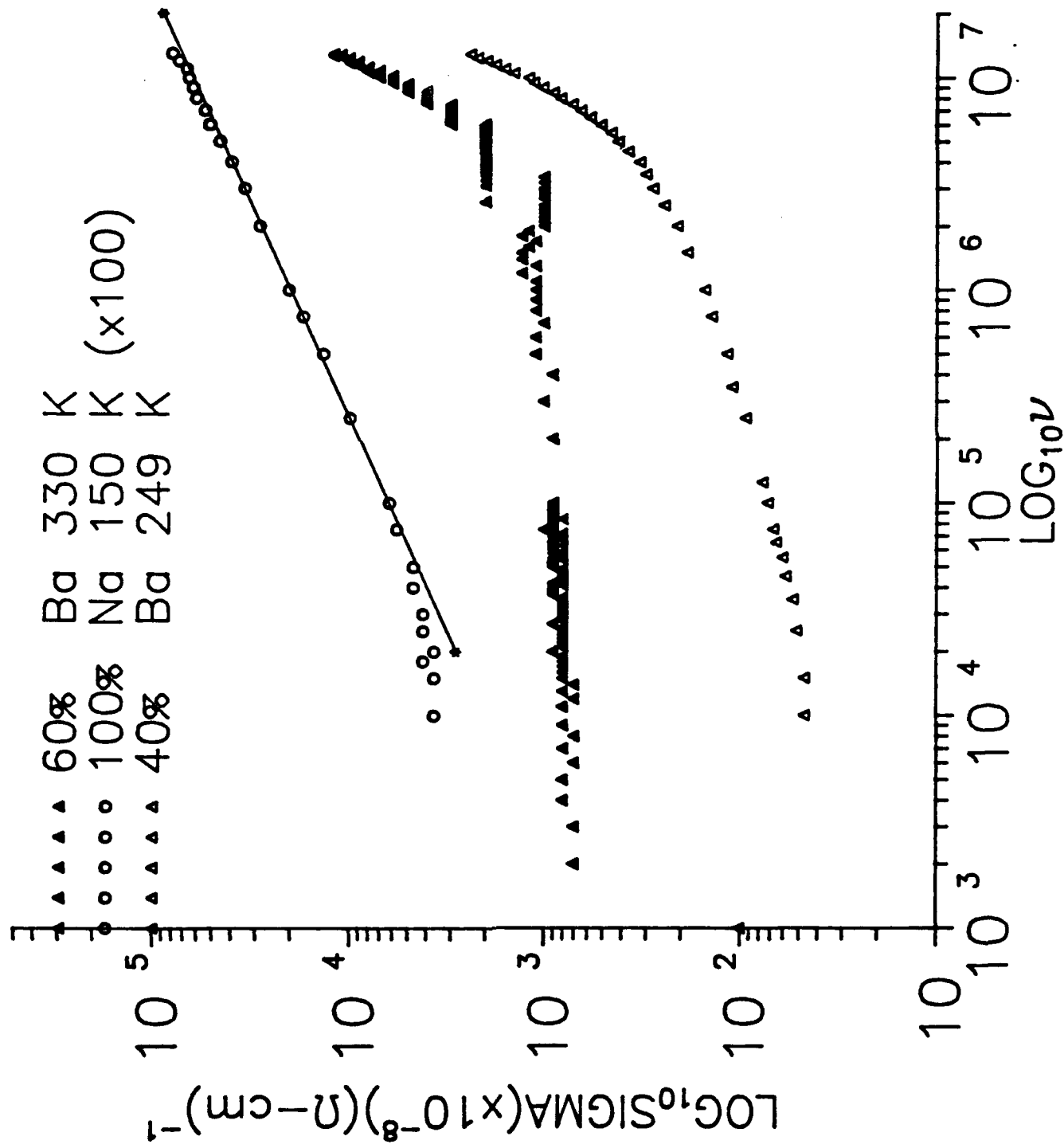
In order to accurately measure the complex conductivity, the probe capacitance in parallel with the sample had to be subtantially smaller than 10^{-14} farads. To achieve this, a pseudo-four probe technique was used. Four matched stainless steel coax were attached directly to the current and voltage leads of the HP4192, and then the current and voltage leads with the same polarity were soldered together close to the sample. Below 10^5 Hz, the accuracy of the measurement was confirmed by

callibration against a General Radio bridge. The temperature was
regulated using a He gas flow system below room temperature, and a
horizontal tube furnace for elevated temperatures.

Results at representative temperatures for $\sigma(\omega)$ for frequencies ω of
the order of the carrier hopping rate for a variety of (Na^+, Ba^{2+})
concentrations are exhibited in Fig.2. The open circles, appropriate to
pure Na^+-β''-alumina at 150K (amplified by 100) exhibit a power law
behavior $Re\sigma(\omega) \sim \omega^{0.5}$ for ω greater than the slowest $1/\tau_{Na}$ (largest Δ_{Na}).
This behavior is typical of most glasses, and is associated with a
distribution of Na^+ hop rates which is divergent at zero hop rate (i.e.
for which the inverse first moment, $\langle 1/(1/\tau)\rangle$ does not exist). The solid
triangles denote $Re\sigma(\omega)$ for 60% Ba^{2+} substitution. As can be seen in
Fig.2, the behavior is very different from the pure material. The
frequency dependence of $Re\sigma(\omega)$ is independent of ω in the low frequency
regime. This implies a much better behaved distribution for the Ba^{2+} hop
rate, with $\langle 1/(1/\tau)\rangle$ finite. A distribution of values for Δ_{Ba} may still
be present, but the behavior of the Ba^{2+} hops is effectively single-
barrier-like. That is, an effective barrier height can be identified,
leading to an effective hop time, $\tau_{eff} = \langle 1/(1/\tau)\rangle$. In Fig. 2, the
associated frequency is about in the middle of the range for the
essentially constant $Re\sigma(\omega)$. Very similar behavior is found for the Na^+-
rich end of the (Na^+, Ba^{2+}) mixtures.

This essentially single particle behavior has other consequences. As
can be seen from Fig.2, there is a crossover to $Re\sigma(\omega) \sim \omega^2$ behavior at
high frequencies. This crossover is usually attributed to the tail of a
high frequency Lorentzian appropriate to oscillations within the potential
well. It is at an unusually low frequency for the mixed materials, and

Fig. 2. Log_{10} $Re\sigma(v)$ vs $Log_{10}(v)$ for 0%, 40%, and 60% Ba^{2+}-exchanged
samples, with similar crossover frequencies from diffusive to
oscillatory motion. The solid lines are power law fits,
$\sigma(v) \sim v^n$, with the values: 0%, $n = 0.5 \pm 0.05$; 40% and 60%,
$n = 2.0 \pm 0.1$.

60% Ba 330 K
100% Na 150 K (x100)
40% Ba 249 K

$LOG_{10}SIGMA(\times 10^{-8})(\Omega-cm)^{-1}$

$LOG_{10}\nu$

may reflect a Ba^{2+}-vacancy mode of vibration. There is no available Raman data to establish the presence of such a low frequency vibrational mode in the mixed materials, so that it would be of some interest to test this hypothesis directly. The absence of a similar ω^2 dependence for the pure material can either be attributed to a much higher vibrational frequency for the Na^+ or Ba^{2+} ions in the pure compound, or to the magnitude of the observed conductivity itself which masks the Lorentzian tail at these frequencies.

The behavior of $Re\sigma(\omega)$ for the 40% Ba^{2+} substitution compound, open triangles in Fig.2, lies mid-way between the pure and the 60% Ba^{2+} material. This concentration is the crossover concentration between the two plateaus. We do not have an adequate picture of dynamics at crossover.

In summary, we have found the ac conductivity of mixed $(Na^+, Ba^{2+})\beta''$-alumina to be markedly different from that of pure Na^+- or Ba^{2+}- β''-alumina. In the "plateau" regions of the activation energy, $\sigma(\omega)$, Cole-Cole plots in the complex impedance plane, and the imaginary part of the electric modulus vs frequency were found to be indicative of uncorrelated single particle hopping, with a single (or small spread in the) effective hopping time, τ_{eff}. For the pure compounds, one finds behavior indicative of a correlated state, arising from an interplay between the single ion potential and the interionic Coulomb repulsive potential. This manifests itself in a power-law dependence for $\sigma(\omega)$ as seen in Fig. 2. We believe this reflects a coupled many-particle state in the pure materials, whereas screening of the interionic Coulomb potential in the mixed materials leads to transport behavior indicative of independent particle motion. It is important to realize that these opposite limits of behavior appear to be

present in the same physical system, appearing in the absence or presence of ionic substitution. Further experiments, especially Raman studies at low shift frequencies, may shed light on the particular vibrational modes which play the major role in ionic transport in these fascinating and important materials.

III. Publications Arising from Research Under Nonr N00014-91-J-1063.

1. M. Underweiser, R. Orbach, S. Adams, and B. Dunn, "Electrical transport of mixed $(Na^+-Ba^{2+})\beta''$-alumina," Phys. Rev. B$\underline{43}$, 11999 – 12003 (1991).

2. M. Underweiser, R. Orbach, S. Adams, and B. Dunn, "A.C. conductivity of mixed $(Na^+-Ba^{2+})\beta''$-alumina," Sol. St. Ionics (in press), (1992).

3. M. Underweiser and R. Orbach, "Frequency dependent electrical conductivity of mixed $(Na^+,Ba^{2+})\beta''$-alumina," in "On Clusters and Clustering: From Atoms to Fractals," Ed. by P.J. Reynolds, in the series "Random Processes and Materials," (North Holland, Amsterdam, 1992). In press.